

Eliminating Cationic Interferences in Chloride Determination via the Mohr Method Using EDTA in Industrial Wastewater Samples

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Abstract

The aim of this study is to modify the Mohr titration method for accurate determination of chloride ions in petroleum wastewater containing interfering cations (Ca^{2+} , Mg^{2+} , Mn^{2+} , and Fe^{3+}), using a pretreatment step with ethylenediaminetetraacetic acid (EDTA). A total of 20 samples were collected from oil well wastewaters in southwestern Iran (Maroon and Azadegan fields). Various volumes of EDTA (1 to 6 mL, 0.02 M) were added to the samples, and chloride was subsequently titrated using the Mohr method. The optimal EDTA volume was determined to be 4 mL per sample. The results indicated that the addition of EDTA to both wastewater and blank samples led to an increase in the volume of titrant (silver nitrate) consumed. Moreover, the titration endpoint in the presence of EDTA was considerably sharper and more clearly distinguishable compared to the standard method. Correlation analysis confirmed a strong relationship between electrical conductivity (EC) and chloride concentration when EDTA was used. Based on the findings, the modified Mohr method with EDTA pretreatment can be recommended as a simple, cost-effective, and accurate protocol for chloride determination in industrial wastewaters with complex matrices.

Keywords: Mohr method, EDTA, Industrial wastewater, Cation chelation, Electrical conductivity

Introduction

Crude oil primarily consists of hydrocarbons and non-hydrocarbons, along with varying amounts of saline water (brine), which causes significant operational challenges such as equipment corrosion, scaling, pressure drop, and increased energy consumption during refining and transportation. The main chloride salts present in crude oil include calcium, magnesium, and sodium chlorides. Various desalting methods exist, but selecting an appropriate, cost-effective technique requires accurate chloride determination. Among standard analytical methods, the Mohr (argentometric) titration is widely used due to its simplicity and low cost. However, its direct application to complex industrial wastewaters is hindered by interfering cations (e.g., Ca^{2+} , Ba^{2+} , Fe^{3+}), which react with the chromate indicator, leading to an obscure endpoint and inaccurate results. To overcome this limitation, the addition of EDTA as a strong chelating agent can effectively mask these cations and restore the accuracy of the Mohr method. This study aims to develop a modified Mohr protocol using EDTA pretreatment to eliminate cationic interferences, providing a simple, precise, and robust method for chloride measurement in industrial wastewater [1, 2, 3, 6].

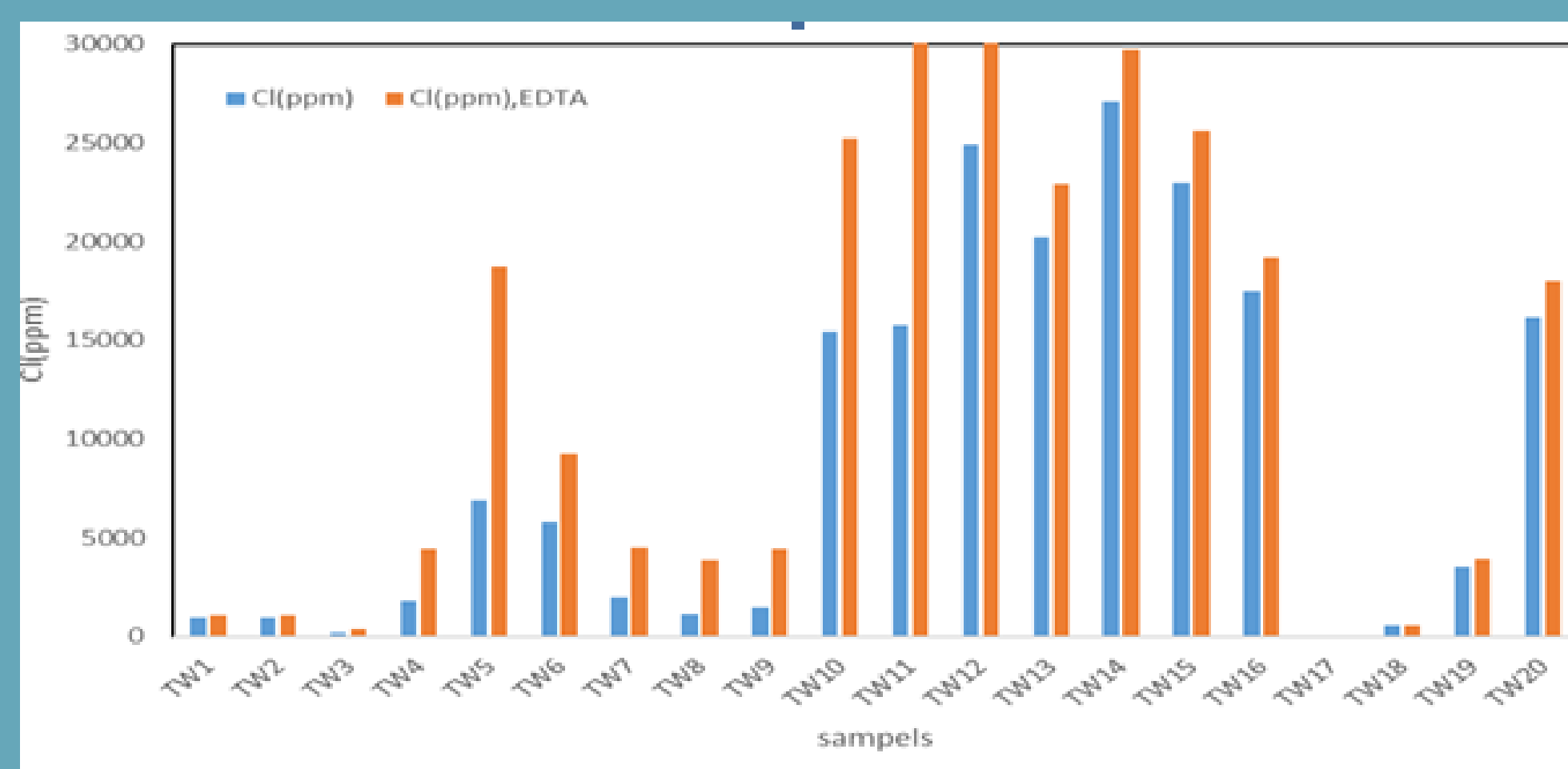


Figure (1): Comparison of chloride values measured in 20 petroleum wastewater samples using the Mohr method with and without EDTA.

Experimental

A modified Mohr titration was developed to determine chloride concentration in 20 oily wastewater samples from Iranian oil fields (Maroon and Azadegan fields). A 25 mL aliquot of each sample was transferred to an Erlenmeyer flask, and 4 mL of 0.02 M EDTA (the optimal volume) was added. The mixture was stirred for 5 minutes to allow complete complexation of interfering cations (Ca^{2+} , Mg^{2+} , Mn^{2+} , Fe^{3+}).

Then, 3 drops of 5% (w/v) potassium chromate (K_2CrO_4) indicator were added, and the solution was titrated with a standardized 0.02 M silver nitrate (AgNO_3) solution until a persistent brick-red endpoint appeared. For comparison, the standard Mohr method (without EDTA) was also performed on all samples. Chloride concentration was calculated using:

$$\text{C}_{\text{Cl}^-} = (\text{V}_{\text{AgNO}_3} \times \text{C}_{\text{AgNO}_3} \times \text{M}_{\text{Cl}^-} / \text{V}_{\text{sample}}) \times 1000$$

EC ranged from 4.04 to 88.75 mS/cm.

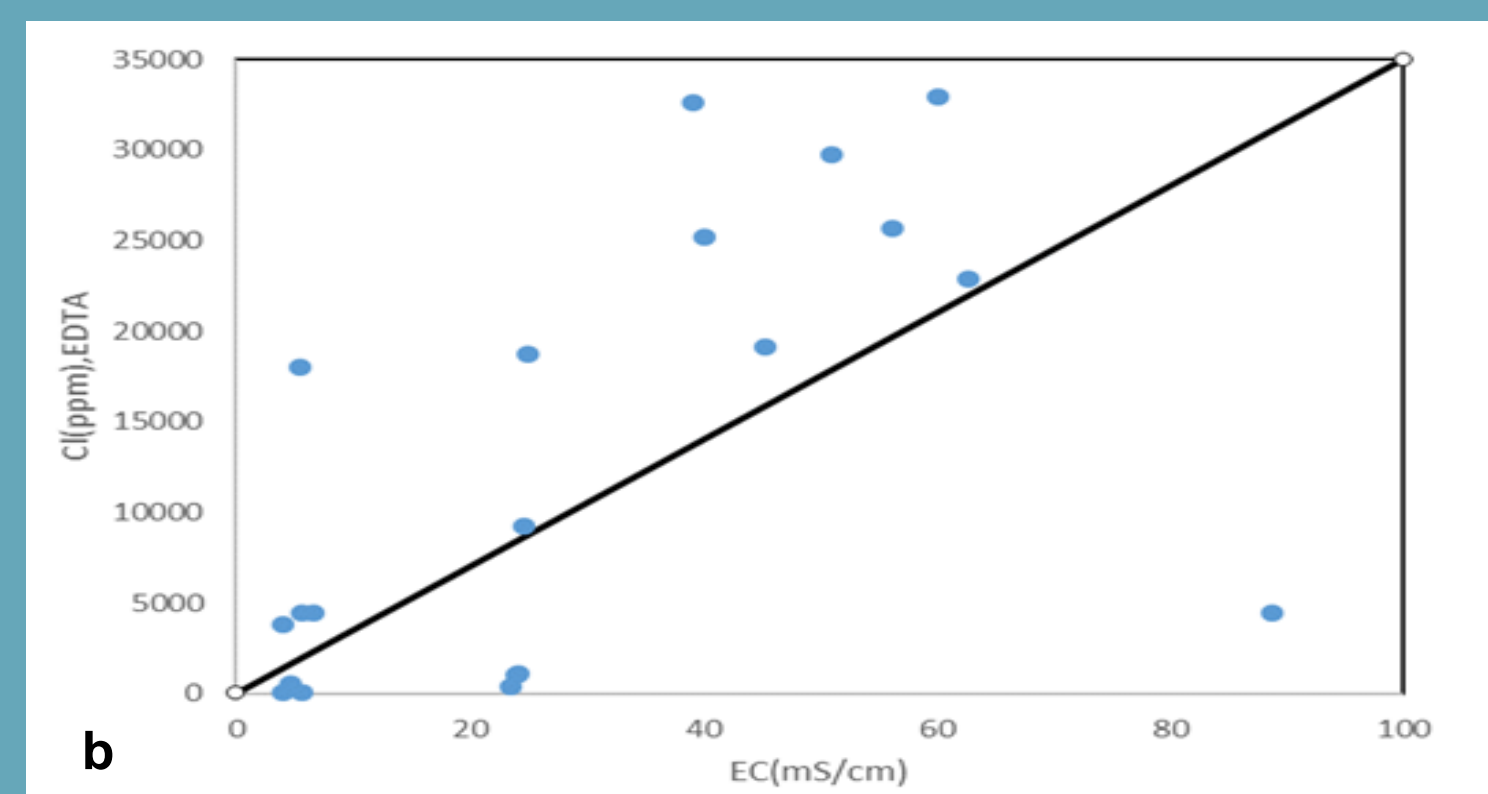
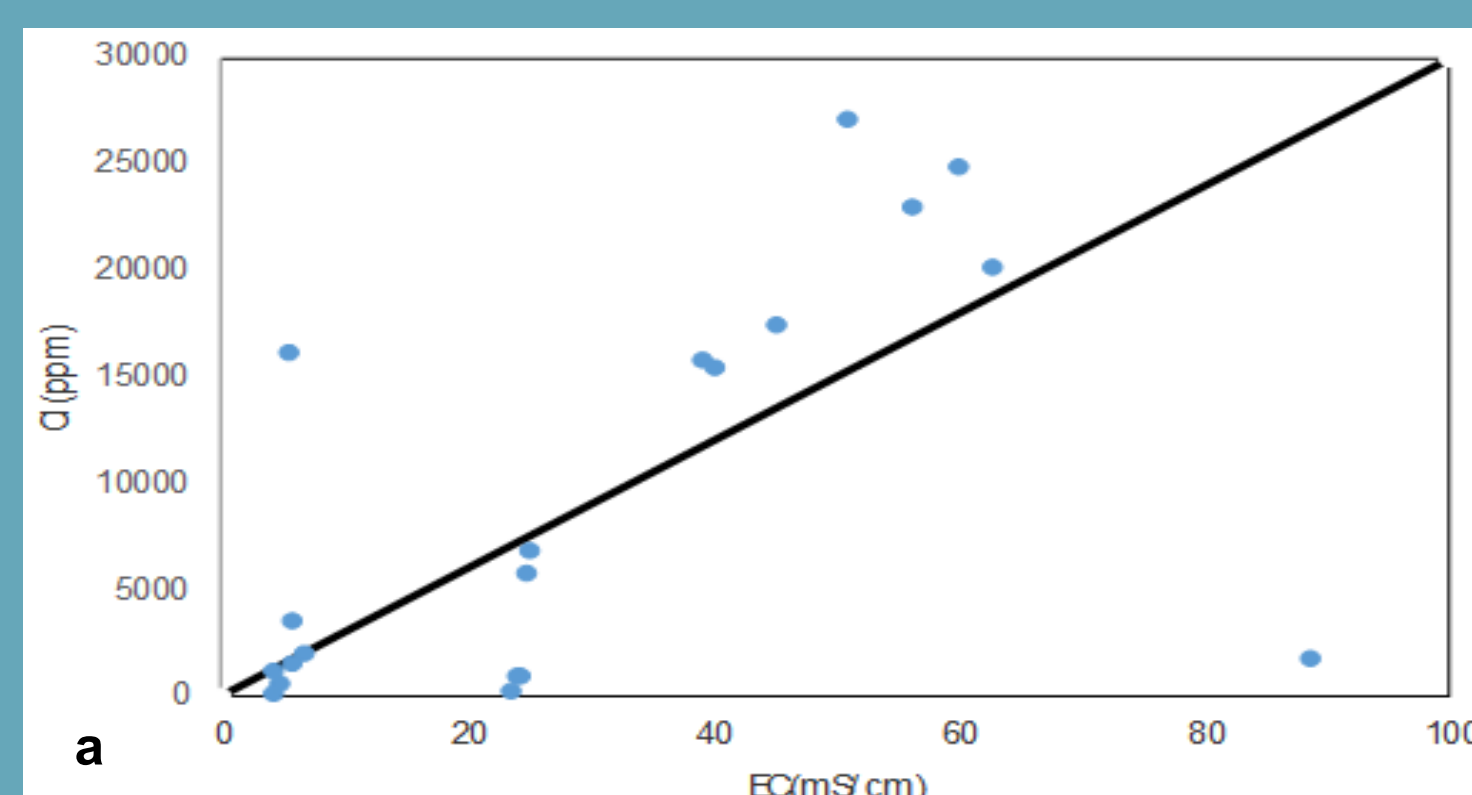


Figure (2): Correlation plots between electrical conductivity (EC) and chloride concentration determined by the Mohr method (a) without EDTA and (b) with EDTA.

Discussion

- ❖ EDTA effectively chelates interfering cations (Ca^{2+} , Mg^{2+} , Mn^{2+} , Fe^{3+}), preventing them from reacting with the chromate indicator.
- ❖ Optimal EDTA volume: 4 mL of 0.02 M solution provided the clearest endpoint.
- ❖ Samples with high EC showed significantly higher chloride values with EDTA pretreatment (Fig. 1), indicating trapped chloride ions were released.
- ❖ Samples with low EC (< 5 mS/cm) and low chloride (< 600 ppm) showed no significant difference, confirming minimal interference.
- ❖ Correlation plots (Figs. 2) confirm a stronger relationship between EC and chloride when EDTA is used, proving chloride is the main contributor to EC[4, 5].

Conclusion

- ✓The EDTA-modified Mohr method effectively eliminates cationic interferences in chloride determination.
- ✓The method is simple, cost-effective, and reliable for complex industrial wastewater samples.
- ✓Chloride measurements with EDTA pretreatment are significantly more accurate, especially in high-EC samples.
- ✓This protocol is recommended as a standard method for chloride analysis in petroleum wastewater and is also applicable to soil and water samples.

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